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Scaled Equation of State and Critical Exponents in Magnets and Fluids

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A systematic analysis in the context of the scaled equation of state has been made of available experimental data in the critical region of a number of ferromagnets [Gd, $CrBr_3$, $La_{0.5}Sr_{0.5}CoO_3$, Ni (two independent sets of data)] and fluids (CO_2, He^4, Xe) with the following assumed form for $h(x)=HM^{-1}|M|^{1-\delta}$:

$$h(x)=E_1[(x+x_0)/x_0]\{1+E_2[(x+x_0)/x_0]^{2\beta}\}^{[\beta(\delta-1)-1]/2\beta},$$

where $h(x)$ is a scaling function, $x=t|M|^{-1/\beta}$, $t=(T-T_c)/T_c$, and $x=-x_0$ is the phase boundary. A nonlinear, least-squares method was used to simultaneously determine the six parameters (β, δ, T_c, x_0, E_1, E_2). Agreement between the proposed form for $h(x)$ and the experimental data was found. For both the magnets and fluids, we find that $\delta\approx4.4$; for the magnets $\beta\approx0.37$ and for the fluids $\beta\approx0.35$. Reasons for the considerably different values reported elsewhere for these exponents in the materials CrO_2 and $YFeO_3$ are discussed.

1. INTRODUCTION

THERMODYNAMIC anomalies in the critical region can be described in terms of power laws which are asymptotically valid as one approaches the critical point. Those of direct concern here are the following:

I. Coexistence curve:

$$M=B(-t)^{\beta}. \tag{1}$$

II. Critical isotherm:

$$H=\Delta\times M|M|^{\delta-1}. \tag{2}$$

III. Susceptibility:

(a) On the critical isochore ($M=0$) $T>T_c$,

$$\chi_T=\Gamma t^{-\gamma}, \tag{3}$$

(b) along the phase boundary $T<T_c$,

$$\chi_T=\Gamma'(-t)^{-\gamma'}. \tag{4}$$

IV. Specific heat at constant magnetization[1]:

(a) $M=0$, $T>T_c$,

$$C_M=(A^+/\alpha)t^{-\alpha}, \tag{5}$$

(b) "two-phase" region $T<T_c$,

$$C_M=(A_{\text{II}}^-/\alpha')(-t)^{-\alpha'}, \tag{6}$$

(c) jump in the specific heat across the phase boundary,

$$\Delta C_M=\Delta_C(-t)^{-\alpha'}. \tag{7}$$

Here t is the reduced temperature $(T-T_c)/T_c$, where T_c is the Curie temperature, H is the internal magnetic field $H_{\text{applied}}-DM$, M is the magnetization, and D is the demagnetizing factor.[2] For fluids analogous relations are found if one chooses the chemical potential $\mu(\rho,t)$ and density ρ as variables and replaces M with $\Delta\rho=(\rho-\rho_c)/\rho_c$ and H with $\Delta\mu=\mu(\rho,t)-\mu(\rho_c,t)$, where ρ_c is the critical density. The susceptibility χ_T then becomes the isothermal compressibility K_T multiplied by the square of the density while C_M becomes ρC_v, C_v being the specific heat at constant volume.

The scaled equation of state[3–5] gives a partial formulation of the thermodynamic properties of the system around the critical point which incorporates all of the anomalies just described. A detailed review, making use of the fluid language, is given in Ref. 6. In the notation of magnetic phenomena[4] the equation of state is written

$$H=M|M|^{\delta-1}h(x), \tag{8}$$

with

$$x=t/|M|^{1/\beta}. \tag{9}$$

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[1] The case $\alpha=0$ can be obtained as

$$\lim_{\alpha\to0}(1/\alpha)(t^{-\alpha}-1)=-\ln t.$$

[2] R. B. Griffiths, J. Appl. Phys. **40**, 1542 (1969).

[3] B. Widom, J. Chem. Phys. **43**, 3898 (1965); L. P. Kadanoff, Physics **2**, 263 (1966).

[4] R. B. Griffiths, Phys. Rev. **158**, 176 (1967).

[5] C. Domb and D. L. Hunter, Proc. Phys. Soc. (London) **86**, 1147 (1965).

[6] M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, J. Res. Natl. Bur. Std. **73A**, 563 (1969).

Here, $h(x)$ is an analytic function of the variable x in the whole range, that is, from $-x_0$ which defines the phase boundary ($x_0=B^{-1/\beta}$) to infinity ($M=0$). Detailed properties of $h(x)$ can be derived from the known behavior of H as a function of M and T and have been reviewed in Ref. 6. We recall that this equation of state leads to equality of the primed and unprimed exponents and to the fulfillment of the thermodynamic inequalities[7–9] as equalities, that is,

$$2-\alpha'=2-\alpha=\beta(\delta+1)\,, \tag{10}$$

$$\gamma'=\gamma=\beta(\delta+1)\,. \tag{11}$$

Now, if the value of two of the exponents were known, experimental H, M, T data could be used to check the validity of Eq. (8) even though the function $h(x)$ is not known to start with. On the other hand, if a closed-form expression for $h(x)$ were available, Eq. (8) could be used to determine the values of the exponents using all available data in the critical region instead of data along preferred curves (critical isotherm, critical isochore, and the phase boundary). The method of preferred curves is the approach that has usually been taken in the past for analyzing experimental data. In particular, for the magnets, analysis of the low-field susceptibility above T_c is used to determine γ and the critical temperature by means of the Kouvel and Fisher technique,[10] henceforth referred to as KF. This method is very attractive. However, it relies upon a determination of the slope of the χ_T^{-1}-versus-T plot which is not very accurate, especially very close to the critical temperature where visual extrapolation of the M^2-versus-H/M curves gives the value of the susceptibility. We shall discuss this point in more detail later.

We have decided to take the other approach using all available data and as the closed-form expression for $h(x)$ the function

$$h(x)=E_1[(x+x_0)/x_0] \times\{1+E_2[(x+x_0)/x_0]^{2\beta}\}^{[\beta(\delta-1)-1]/2\beta}, \tag{12}$$

where β, δ, x_0, E_1, E_2, and implicitly T_c are adjustable constants. This function gave a good fit to the data in the fluid case where the exponent β and the value of the parameter x_0 were assumed to be independently known from an analysis of the phase boundary.[6,11] This assumed form for the function $h(x)$ satisfies the following requirements of scaling: (a) $h(x)$ is analytic everywhere, $-x_0<x<\infty$; (b) $h(-x_0)=0$, the derivative, $h'(-x_0)$ finite, $\chi_T(-x_0)$ defined; (c) $\beta\delta h(x)\geqq xh'(x)$, $x>-x_0$, χ_T positive; (d) $h''(x)\geqq 0$, sufficient for $C_M>0$. For large values of $x(M\rightarrow 0)$ the function $h(x)$ has the series expansion

$$h(x)=x^{\gamma}\Big[\sum_{n=0}^{\infty}\eta_n x^{-2\beta n}+\sum_{n=1}^{\infty}\xi_n x^{-n}\Big]. \tag{13}$$

The second series on the right-hand side of Eq. (13) gives spurious terms, the first of which is proportional to $x^{\gamma-1}$. Since experimentally it appears that $2\beta<1$, but $4\beta>1$, this spurious term will then be the third term in the large x expansion of $h(x)$. Consequently, this function will not give the correct behavior of the higher-order derivatives of H with respect to M. We will discuss this point in detail later.

Equation (12) has the advantage of giving a closed form for $h(x)$ with a relatively small number of adjustable parameters: β, δ, x_0, E_1, E_2, and implicitly T_c, which is suitable for a multiparameter fit of the experimental data.

2. DATA ANALYSIS

The multiparameter (nonlinear) fit to the experimental H, M, T data was done using Eq. (8) with $h(x)$ given by Eq. (12), by employing the maximum neighborhood technique developed by Marquardt.[12] This procedure combines features of the Taylor series expansion method with properties of the method of steepest descents to construct an algorithm which determines at each iteration the range over which a linearized function will give an adequate representation of a nonlinear function. In this procedure, an initial guess of the (many) parameters to be evaluated must be given. In actual practice we have found that depending on the number of experimental data points available, and their distribution in the critical region, different initial guesses for the parameters would, or would not, converge to the same final answer. In general, the different final values for the parameters were in agreement within the standard error given by the nonlinear fit (which was evaluated assuming linearity). Once the successive iterations remained within the standard error limits, convergence was accelerated by taking the average of a suitable number of already obtained values as initial guess. Only very few iterations were then needed to stabilize the parameter values completely. Moreover, a detailed analysis of the deviations of the experimental points from the calculated function showed that truly systematic deviations appeared when the parameters were varied outside of their standard error range. Accordingly, the procedure we adopted was to study the convergence for many different sets of initial guesses of the parameters for every substance studied. We then chose the common value or the average obtained from the various fits as the most probable value of each parameter and assigned to it as an error the standard error given by the multiparameter fit itself.

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[7] R. B. Griffiths, J. Chem. Phys. **43**, 1958 (1965); Phys. Rev. Letters, **14**, 623 (1965).

[8] G. S. Rushbrooke, J. Chem. Phys. **39**, 842 (1963); **43**, 3439 (1965).

[9] M. E. Fisher, J. Math. Phys. **5**, 944 (1964).

[10] J. S. Kouvel and M. E. Fisher, Phys. Rev. **136**, A1626 (1964).

[11] M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, Phys. Rev. Letters **22**, 389 (1969).

[12] D. W. Marquardt, J. Soc. Ind. Appl. Math. **11**, 431 (1963).

Weights were assigned to H, M, and t according to the reported precision of the experimental data. The fit was done assuming the variable x free of error, and through propagation of errors the quantity $[h(x)]_{\text{expt}} = H/M|M|^{\delta-1}$ was weighted according to

$$w_h = \{(\sigma_h/H)^2 + (\sigma_M/M)^2[\delta - x/\beta(x+x_0)]^2 + (\sigma_t^2/t)[x/(x+x_0)]^2\}^{-1}[h(x)]_{\text{expt}}^{-2}, \quad (14)$$

where the σ are the appropriate errors in the experimental quantities.

A reasonable amount of experimental information was available to us for the following substances:

Magnets: Ni,[13] Ni,[14] Gd,[15] CrO_2,[16] $CrBr_3$,[17] $La_{0.5}Sr_{0.5}CoO_3$,[18] and $YFeO_3$.[19]

Fluids: CO_2,[20] Xe,[21] and He^4.[22]

A detailed discussion of the derivation of the chemical potential-density data for the fluids from the pressure-volume isotherms together with the appropriate numerical values of $\Delta\mu$ and $\Delta\rho$ and an analysis of their errors is given in Ref. 6. Reducing factors for the density and chemical potential are given there in terms of the critical parameters. For the magnetic substances we used reduced units for the magnetization and the magnetic field. The reducing factor used for the magnetization was the approximate value of the saturation magnetization M_0 at 0 K and for the field the quantity k_BT_c/m, where k_B is Boltzmann's factor and m the magnetic moment per spin. For the magnetic substances the reducing factors used are given in Table I. The internal field was derived from the applied field using the demagnetizing factor D given by the respective authors in Refs. 13–19. A variation of D around these values was shown not to significantly influence the results of the fit.

Obviously in order to obtain information on the critical-point behavior one needs to have experimental data as close as possible to the critical point. In order to gain some insight into how close the data for the various substances are we have used approximate values for x_0, β, and T_c to construct "Widom plots,"[3] t versus $x_0|M|^{1/\beta}$, and these are shown for some of the materials in Figs. 1(a) and 1(b). In these plots, the straight line at 45° in the lower quadrant represents the phase boundary, the one-phase region being the upper unshaded area. For each substance the line represents the closest approach to the critical region, that is, experimental data were available above and to the right of the appropriate line. Ideally one would like to have a large number of data points inside a circular region of some small radius about the origin. In Fig. 1(a), it is seen that the amount of information one can obtain from the two sets of Ni data, and the data on Gd and $CrBr_3$ is comparable. For the case of $La_{0.5}Sr_{0.5}CoO_3$ on the other hand, it is clear that the results will be less reliable. There is only one isotherm below critical, $t<0$, for the present choice of T_c; also, the experimental data are considerably further removed from the critical point than in the other cases. We have not included on this plot the data for CrO_2 because there is evidence[23] that close to the Curie point magnetocrystalline anisotropy severely affects the data. As to the $YFeO_3$ data, they are indeed very close to the critical point, but as Heller[24] has pointed out, this material is really an antiferromagnet and what is actually measured is the product of canting angle and sublattice magnetization. The canting angle is known only[25] to be constant below 0.99 T_c which is outside of the range of the present measurements and hence it is doubtful that these measurements give the true behavior of the magnetization. In fact, if one plots M^2 versus H/M for these data one finds an upwards curvature rather than the usually observed downwards curvature. From Fig. 1(b) it is seen that for He^4 the spacing in temperature is far better than for CO_2 and Xe (for Xe no subcritical isotherms are available), but for the latter two cases, the approach to the critical point as far as $\Delta\rho$ is concerned is somewhat better. Consequently, the nonlinear method of fitting the data was applied to the data for all the materials except $YFeO_3$.

TABLE I. Magnetization and field reducing factors.

	Magnetization (M_0 in emu/g)	Field k_BT_c/m in Oe$\times 10^{-6}$
$CrBr_3$	1	0.163
Gd	69.974	1.526
Ni	58.6	15.16
$La_{0.5}Sr_{0.5}CoO_3$	40	8.0

Since what we are trying to establish is the asymptotic behavior in the critical region, a "cutoff" line defining the extent of the asymptotic region in Figs. 1(a) and 1(b) is then needed. However, nothing is *a priori* known on this subject, and hence one can only guess the form that line might take. One method of proceeding would be to assume that this region extends to some maximum value of the magnetization. For isotherms very close to the critical isotherm this is equivalent to a maximum field cutoff, but for isotherms further from critical, this is not the case. We have therefore decided

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[13] P. Weiss and R. Forrer, Ann. Phys. (Paris) **5**, 153 (1926).

[14] J. S. Kouvel and J. B. Comly, Phys. Rev. Letters **20**, 1237 (1968).

[15] C. D. Graham, Jr., J. Appl. Phys. **36**, 1135 (1965).

[16] J. S. Kouvel and D. S. Rodbell, J. Appl. Phys. **38**, 979 (1967).

[17] J. T. Ho and J. D. Litster, Phys. Rev. Letters **22**, 603 (1969); J. Appl. Phys. **40**, 1270 (1969).

[18] N. Menyuk, P. M. Raccah, and K. Dwight, Phys. Rev. **166**, 510 (1968).

[19] G. Gorodetsky, S. Shtrikman, and D. Treves, Solid State Commun. **4**, 147 (1966).

[20] A. Michels, B. Blaisse, and C. Michels, Proc. Roy. Soc. (London) **A160**, 358 (1937).

[21] H. W. Habgood and W. G. Schneider, Can. J. Chem. **42**, 98 (1954).

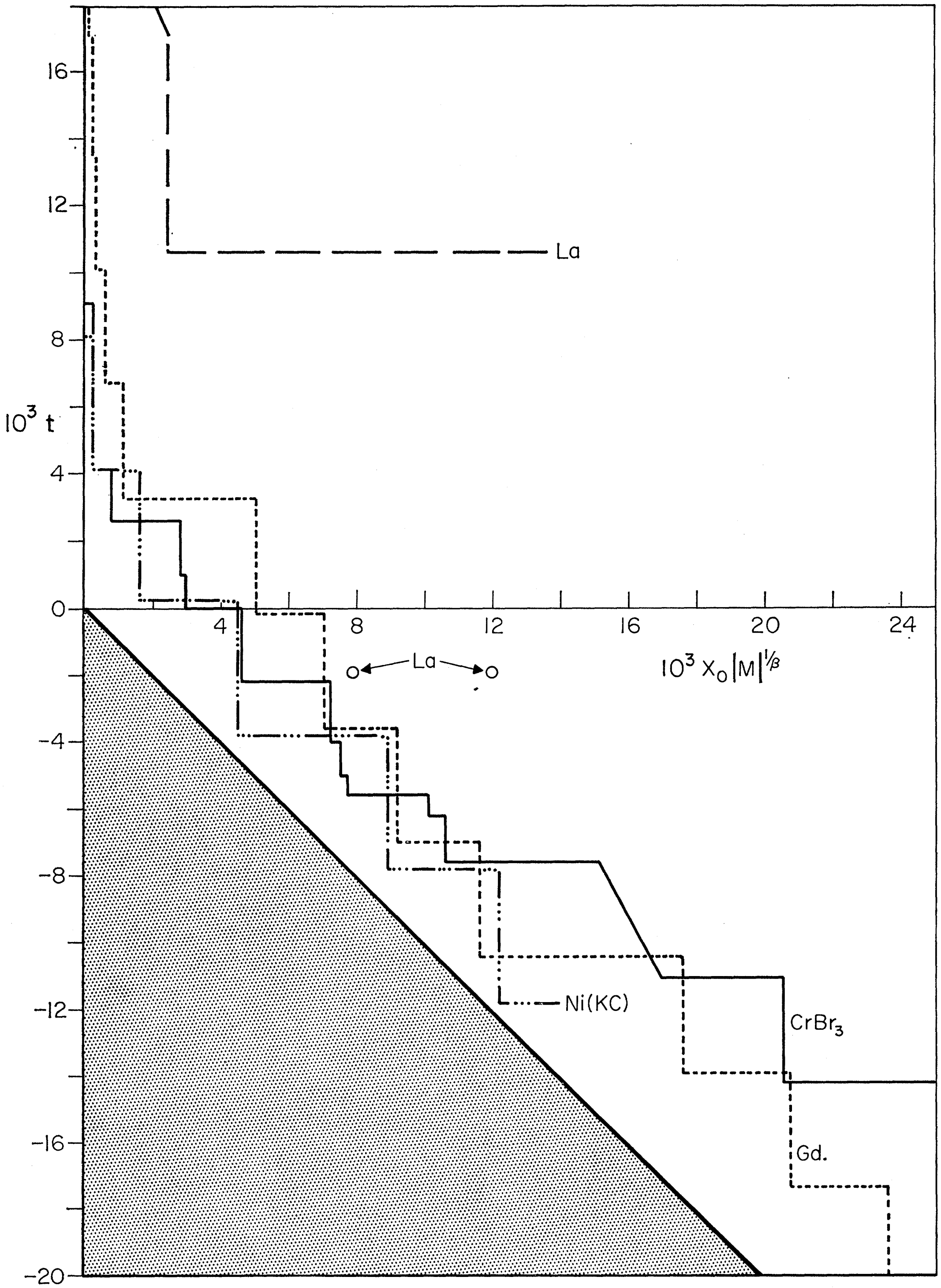
[22] P. R. Roach, Phys. Rev. **170**, 213 (1968).

[23] D. S. Rodbell, J. Phys. Soc. Japan **21**, 1224 (1966).

[24] P. Heller, Rept. Progr. Phys. **30**, 731 (1967).

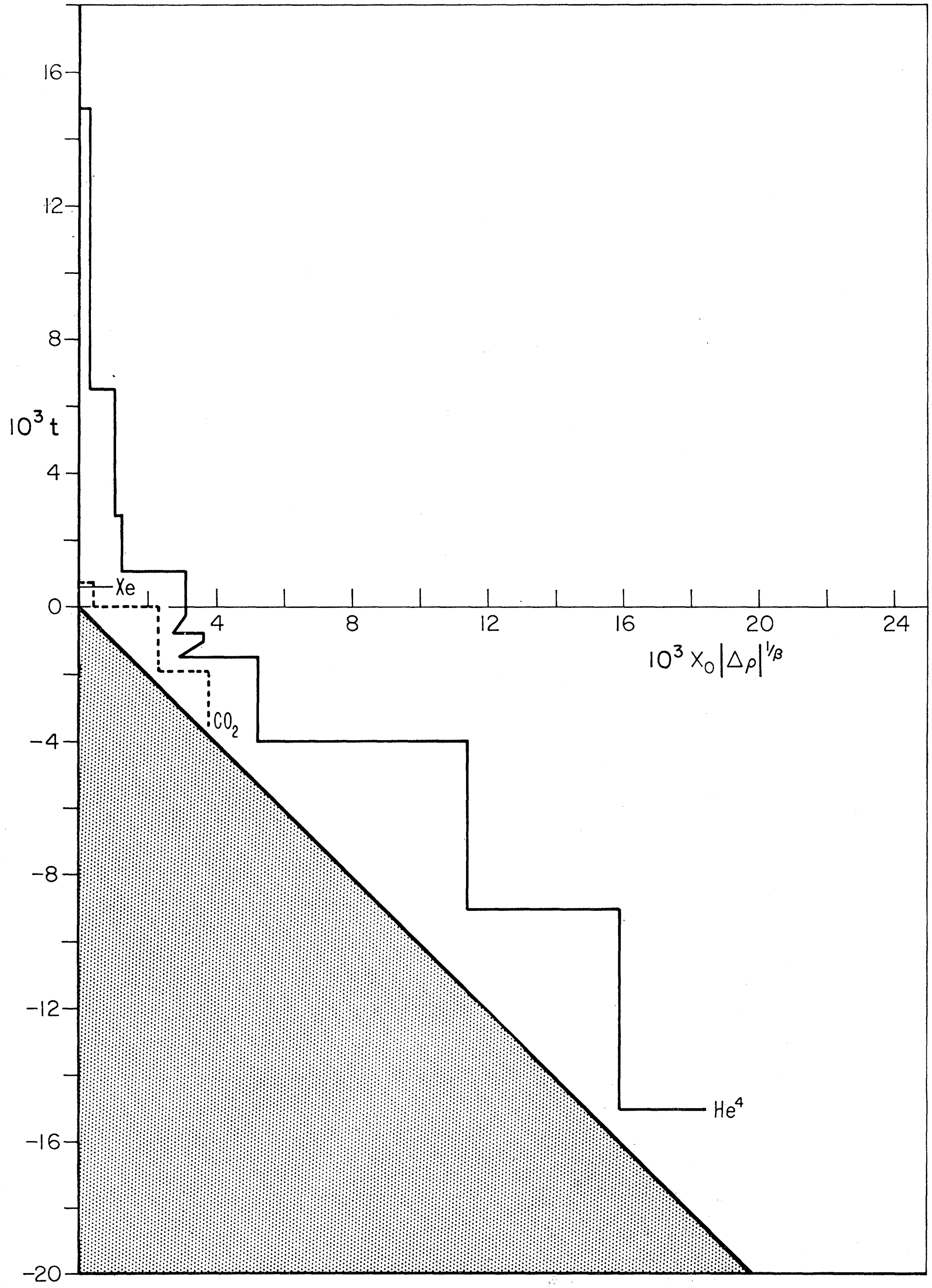
[25] D. Treves, J. Appl. Phys. **36**, 1033 (1965).

to systematically disregard points at large fields and large magnetization. The data were assumed to be in the true asymptotic region when further reduction of the range in which the data points were taken did not affect the values of the derived parameters. It was thus found that points with $M \geq 0.35-0.40$ were outside of



(a)

FIG. 1. (a) Widom plot (t versus $x_0|M|^{1/\beta}$) for various magnets. (b) Widom plot (t versus $x_0|\Delta\rho|^{1/\beta}$) for various fluids.



(b)

FIG. 1 (*continued*)

this range for all temperatures and that the range in M at temperatures not close to critical was smaller.

Figures 2(a)–7(a) show the results of our analysis for all the magnets and fluids considered except Xe, $La_{0.5}Sr_{0.5}CoO_3$, and CrO_2. What is shown on a log-log plot is a comparison between the derived $h(x)$ (solid

TABLE II. Derived parameters $[T_c(\mathrm{K}),x_0,\beta,\delta,E_1,E_2]$ in the critical region for magnets and fluids. Exponent γ is obtained from Eq. (11). For magnets numbers in parentheses are those reported by authors mentioned in text (see Refs. 10, 14, 15, 17, and 18). Values of γ marked by † are obtained for the given values of δ and β by Eq. (11). For fluids numbers in parentheses are results of four-parameter fit (see Ref. 6).

	T_c(K)	x_0	β	δ	E_1	E_2	γ
$CrBr_3$	32.841 ±0.008	0.596±0.010	0.364±0.005	4.32±0.10	0.55±0.02	0.64 ±0.03	1.21
	(32.844)	(0.609±0.009)	(0.368±0.005)	(4.28±0.10)			(1.215±0.020)
Gd	292.05 ±0.15	0.670±0.050	0.370±0.010	4.39±0.10	0.70±0.10	0.97 ±0.10	1.25
	(292.5 ±0.5)		(0.44 ±0.04)†	(4.0 ±0.1)			(1.33)
Ni[a]	627.4 ±0.3	0.376±0.047	0.373±0.016	4.44±0.18	0.19±0.04	0.77 ±0.06	1.28
	(627.4)		(0.378±0.004)†	(4.58±0.05)			(1.34 ±0.01)
Ni[b]	626.5 ±0.2	0.363±0.030	0.375±0.013	4.48±0.14	0.18±0.03	0.83±0.08	1.31
	(627.2)		(0.404±0.020)†	(4.22±0.03)			(1.35 ±0.02)
$La_{0.5}Sr_{0.5}CoO_3$	227.7	0.618	0.37	4.39	0.022	18.5	1.26
	228.4	0.144	0.63	3.0	0.006	7.9	1.26
	(228.4)		(0.62 ±0.03)†	(3.05±0.06)			(1.27 ±0.02)
CO_2	304.12 ±0.04	0.139±0.011	0.352±0.008	4.47±0.12	2.14±0.16	0.300±0.15	1.22
	(304.10 ±0.04)	(0.135)	(0.350)	(4.6 ±0.1)	(2.36±0.02)	(0.30±0.02)	(1.26)
Xe	289.73 ±0.04	0.18 ±0.06	0.35 ±0.07	4.6 ±0.5	2.7 ±0.9	0.36 ±0.13	1.26
	(289.73 ±0.03)	(0.186)	(0.350)	(4.6 ±0.1)	(2.96±0.07)	(0.37 ±0.03)	(1.26)
He^4	5.1874±0.0011	0.369±0.018	0.355±0.009	4.44±0.10	2.80±0.25	0.41 ±0.06	1.24
	(5.1884±0.0008)	(0.360)	(0.359)	(4.45±0.10)	(2.78±0.03)	(0.48 ±0.03)	(1.24)

[a] Reference 14.
[b] Reference 13.

line) and the experimental $h(x)$ (points). Since this sort of plot conceals systematic deviations, we have plotted in Figs. 2(b)–7(b) the corresponding relative deviations themselves, $\{[h(x)]_{\mathrm{expt}}-[h(x)]_{\mathrm{fitted}}\}/[h(x)]_{\mathrm{expt}}$.

The vertical lines in these figures represent the experimental uncertainties. The "best-fit" parameters are listed in Table II and will be discussed in detail shortly.

As mentioned previously, the CrO_2 data are severly affected by magnetocrystalline anisotropy for $M\leqq 0.40$. Consequently Kouvel and Rodbell[16] attempted to analyze their data only at larger magnetizations, which, we feel, would be outside of the asymptotic region. Hence we believe that the parameters they obtained are not characteristic of this substance. We have attempted to scale their lower magnetization data, but with no success. In regard to $La_{0.5}Sr_{0.5}CoO_3$ and Xe it is obvious from Figs. 1(a) and 1(b), respectively, that considerable difficulties should be anticipated in an attempt at fitting, since information concerning subcritical temperatures is very poor. This explains the very large errors we found for Xe. In Figs. 8(a) and 8(b) we show a typical fit for Xe for the parameters given in Table II. In the case of $La_{0.5}Sr_{0.5}CoO_3$ the program could not be made to work properly when all six parameters were allowed to vary simultaneously. Therefore we decided to fix the values of the parameters β and δ and allow only the remaining four to vary. Choosing $\beta=0.63$, $\delta=3$, as given in the original analysis,[18] we obtain a good fit, as displayed in Figs. 9(a) and 9(b). However, taking $\beta=0.37$, $\delta=4.4$ close to the values for the other magnetic substances, we obtain an equally satisfactory fit, as shown in Figs. 10(a) and 10(b). The corresponding values of the other parameters for the two cases are given in Table II. The significance of these results will be discussed below.

3. RESULTS

The plots of log $h(x)$ versus $\log[(x+x_0)/x_0]$ for all substances [Figs. 2(a)–10(a)] show good agreement between the fit of the proposed function, Eq. (12), and the experimental points. A more satisfactory way of looking at this agreement is given by the deviation plots of Figs. 2(b)–10(b). No general statement can be made about systematic behavior of the deviations on a given isotherm. In this respect, the only case for which there appears to be any evidence for systematic deviations is given by the fit of the $CrBr_3$ data, Fig. 2(b). However, as is evident from Table II, the values of the parameters x_0, T_c, β, and δ are in good agreement with the values given by Ho and Litster.[17] Moreover, in the analysis of their data these authors have also derived value for the first coefficients in the series expansion of $h(x)$ near the critical isotherm

$$h(x)=h_0+h_1x+h_2x^2+\cdots, \tag{15}$$

as well as the first three coefficients in the expansion valid near the critical isochore

$$h(x)=\eta_1x^{\gamma}+\eta_2x^{\gamma-2\beta}+\eta_3x^{\gamma-4\beta}. \tag{16}$$

We can also derive these coefficients by expansion of our function Eq. (12), and a comparison between these values is given in Table III. We note that the agreement is good for the values of h_0, h_1, and η_1. The discrepancy in h_2 can be explained by the fact that Ho and Litster assume h_m, $m\geq 3$, to be rigorously zero, while the difference between our η_2 and η_3 and theirs is obviously due to the presence of the first spurious term proportional to $x^{\gamma-1}$ in the large-x expansion of our function. We then conclude that as far as the prediction of all exponents and of the leading terms in the behavior on the critical isotherm (h_0,h_1) and on the critical isochore (η_1)

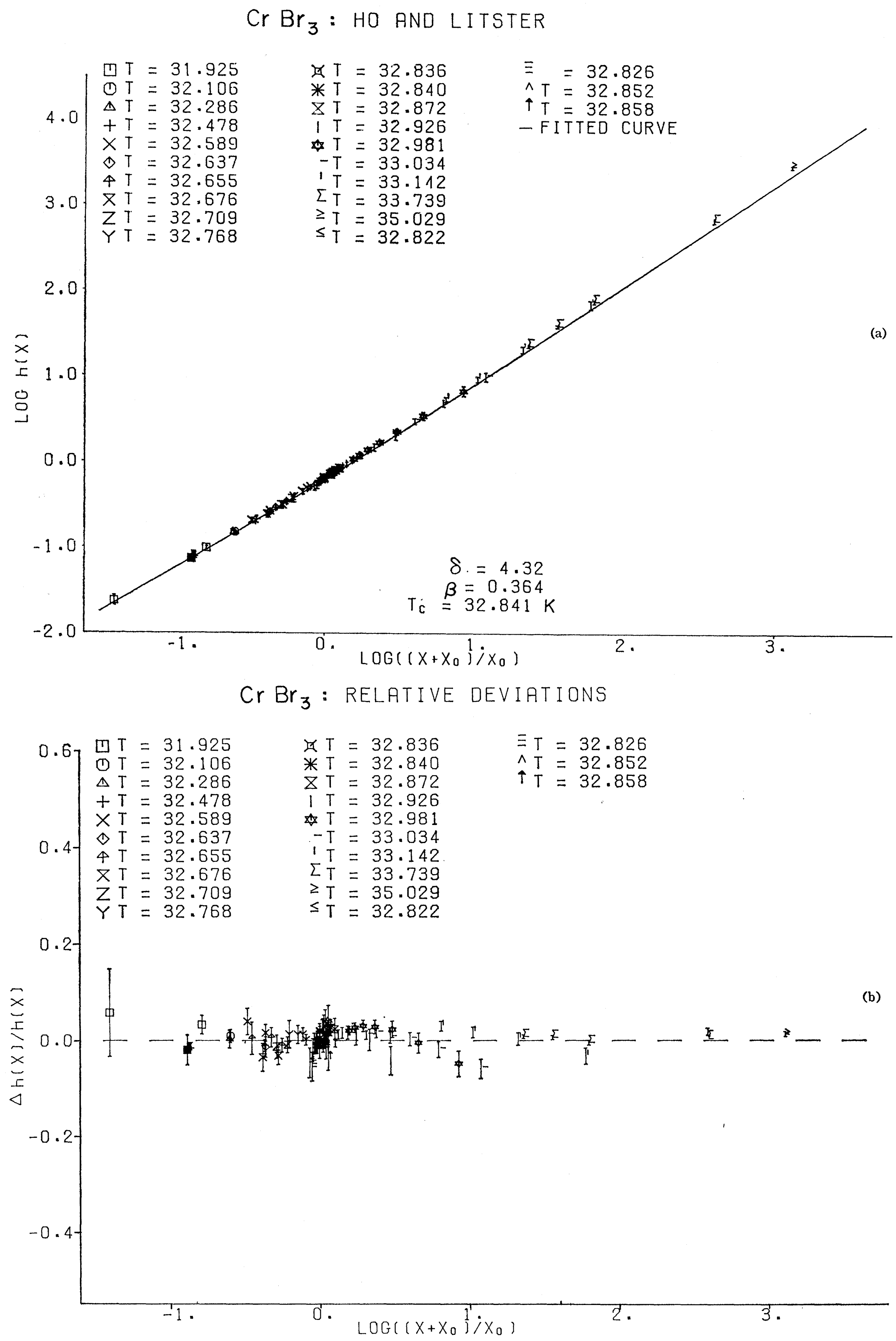


FIG. 2. (a) Log-log plot of $h(x)$ versus $(x+x_0)/x_0$ for CrBr$_3$. Solid line is fitted function [Eq. (12)] with parameters given in Table II. Experimental points are shown with estimated error bars on variable $h(x)$. (b) Plot of $\Delta h(x)=\{[h(x)]_{\text{expt}}-[h(x)]_{\text{fitted}}\}/[h(x)]_{\text{expt}}$ versus $\log[(x+x_0)/x_0]$ for CrBr$_3$. Vertical error bars include all experimental uncertainties.

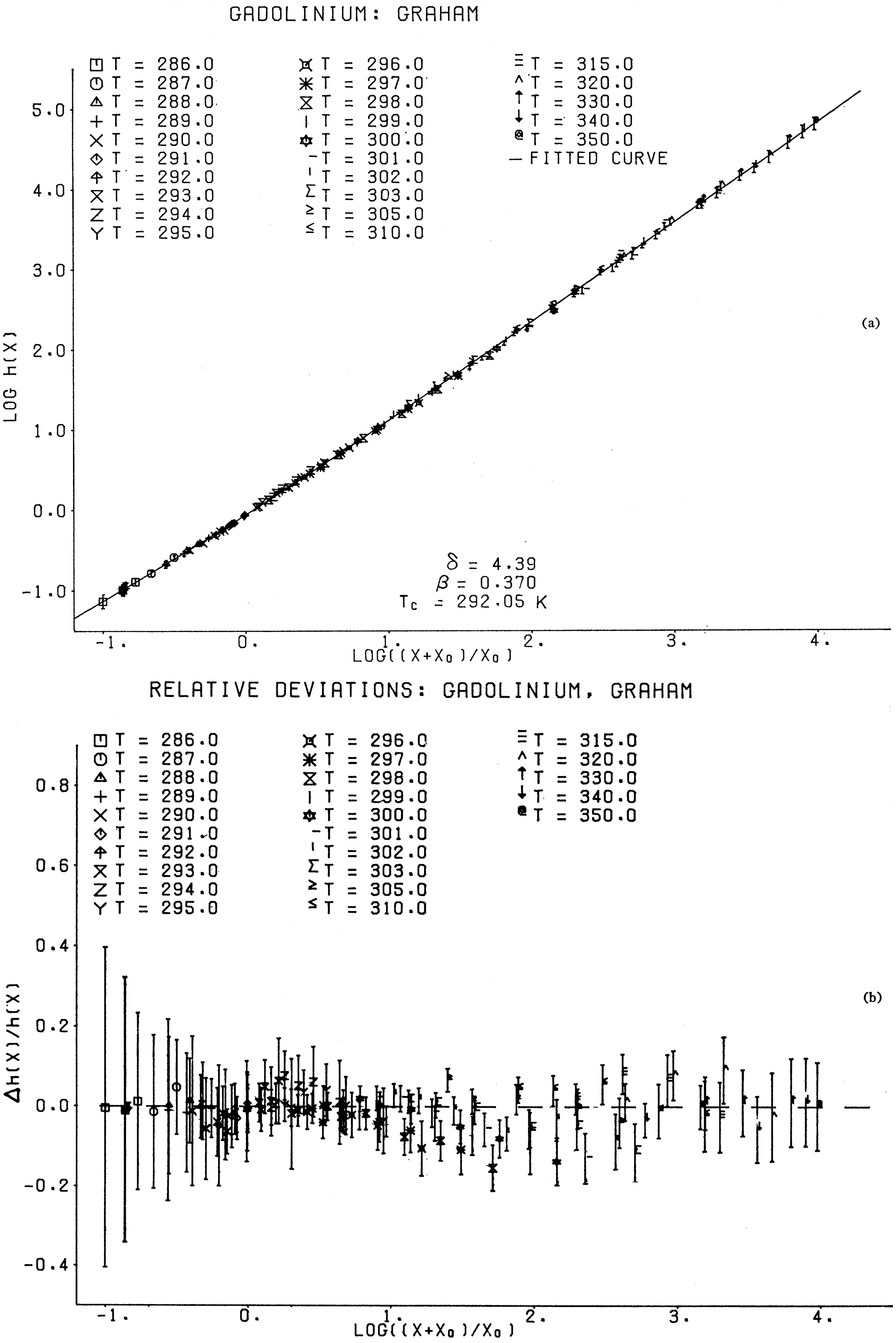


FIG. 3. (a) Log-log plot of $h(x)$ versus $(x+x_0)/x_0$ for Gd. Solid line is fitted function [Eq. 12)] with parameters given in Table II. Experimental points are shown with estimated error bars on variable $h(x)$. (b) Plot of $\Delta h(x)=\{[h(x)]_{\text{expt}}-[h(x)]_{\text{fitted}}\}/[h(x)]_{\text{expt}}$ versus $\log[(x+x_0)/x_0]$ for Gd. Vertical estimated error bars include all experimental uncertainties.

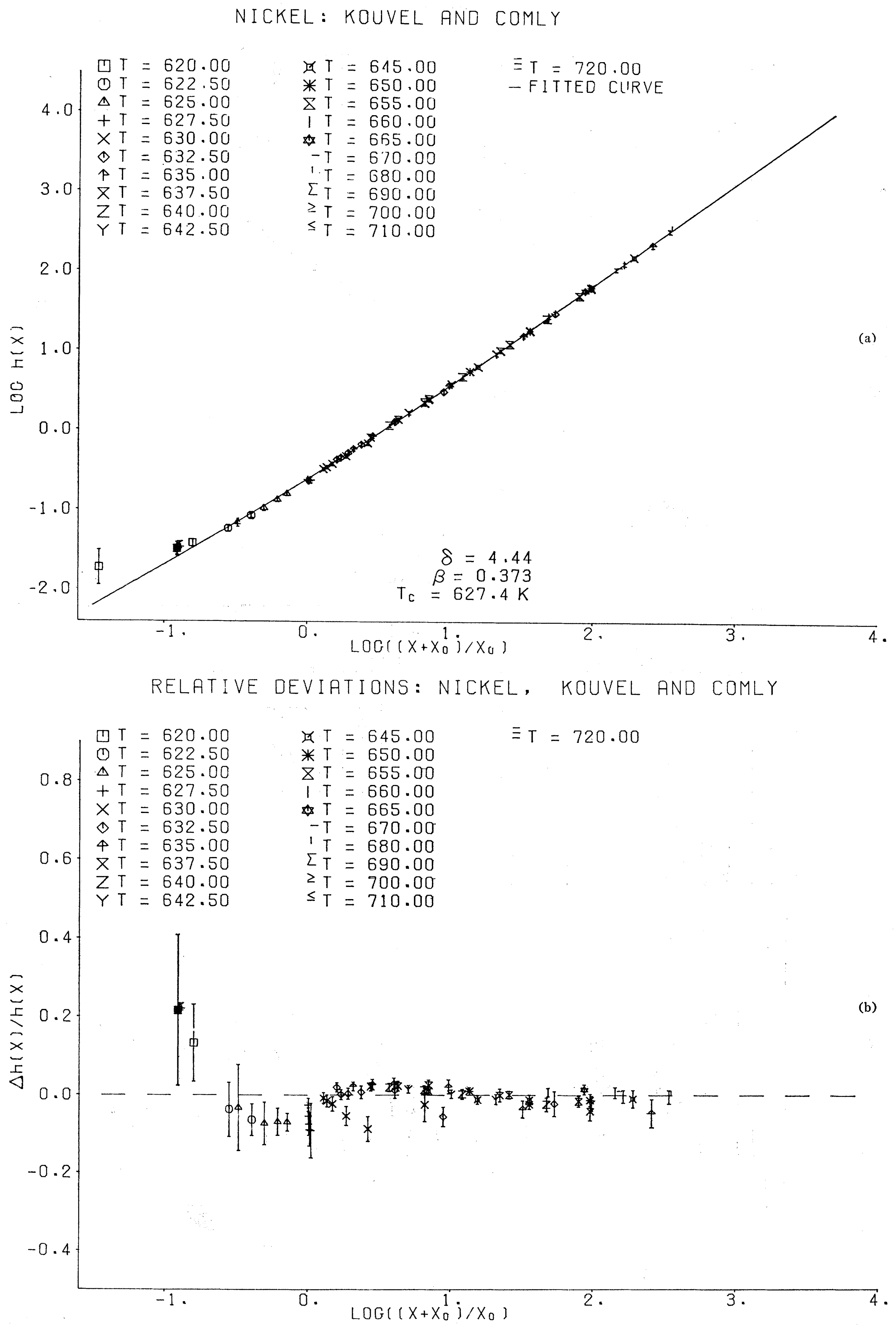


FIG. 4. (a) Log-log plot of $h(x)$ versus $(x+x_0)/x_0$ for Ni (Ref. 14). Solid line is fitted function [Eq. (12)] with parameters given in Table II. Experimental points are shown with estimated error bars on variable $h(x)$. (b) Plot of $\Delta h(x)=\{[h/x)]_{\mathrm{expt}}-[h(x)]_{\mathrm{fitted}}\}/[h(x)]_{\mathrm{expt}}$ versus $\log[(x+x_0)/x_0]$ for Ni (Ref. 14). Vertical error bars include all experimental uncertainties.

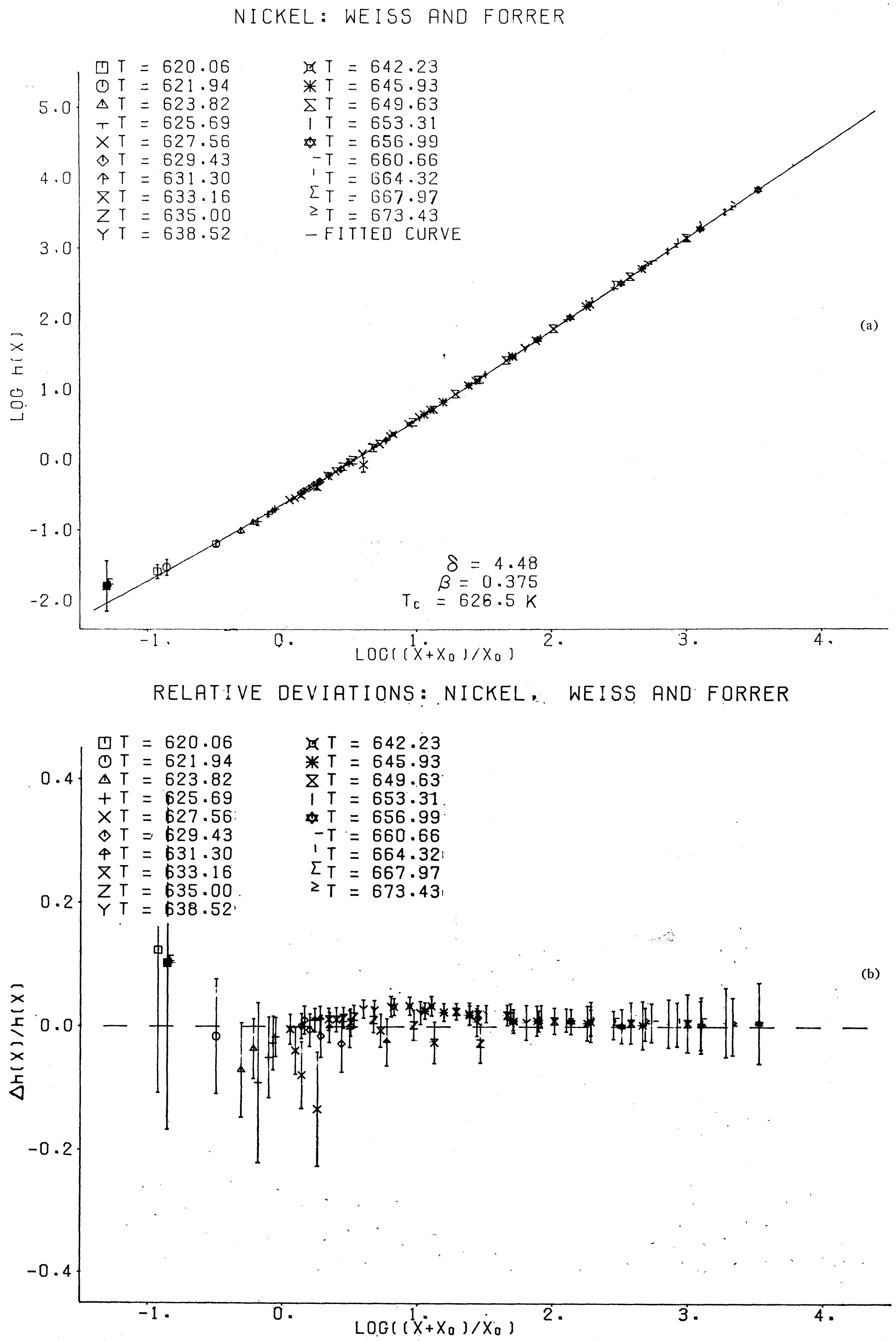


FIG. 5. (a) Log-log plot of $h(x)$ versus $(x+x_0)/x_0$ for Ni (Ref. 13). Solid line is fitted function [Eq. (12)] with parameters given in Table II. Experimental points are shown with error bars on variable $h(x)$. (b) Plot of $\Delta h(x)=\{[h(x)]_{\mathrm{expt}}-[h(x)]_{\mathrm{fitted}}\}/[h(x)]_{\mathrm{expt}}$ versus $\log[(x+x_0)/(x_0]$ for Ni (Ref. 13). Vertical error bars represent estimated limits that include all experimental uncertainties.

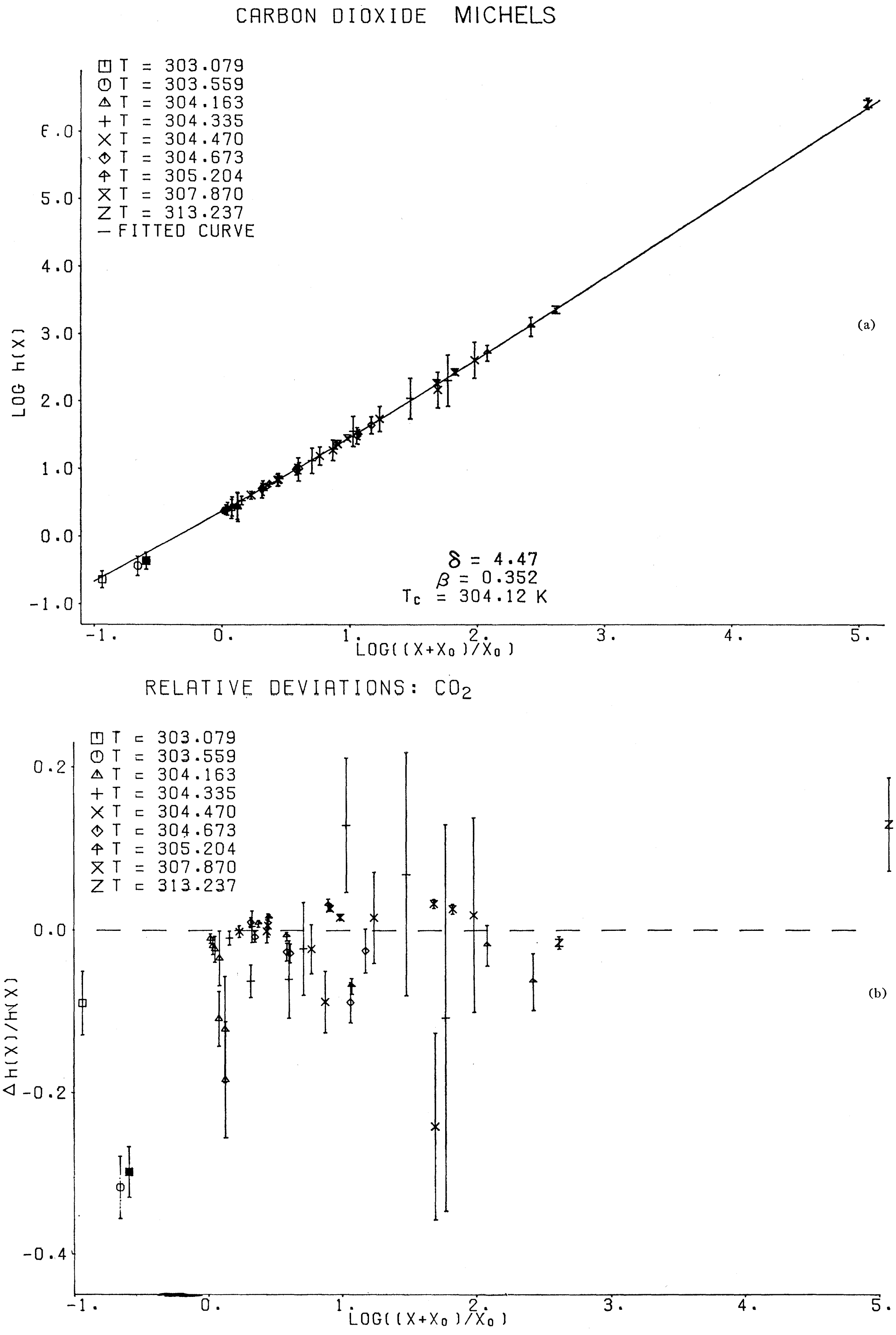


FIG. 6. (a) Log-log plot of $h(x)$ versus $(x+x_0)/x_0$ for CO_2. Solid line is fitted function [Eq. (12)] with parameters given in Table II. Experimental points are shown with estimated error bars on variable $h(x)$. (b) Plot of $\Delta h(x)=\{[h(x)]_{\text{expt}}-[h(x)]_{\text{fitted}}\}/[h(x)]_{\text{expt}}$ versus $\log[(x+x_0)/x_0]$ for CO_2. Vertical error bars represent estimated limits that include all experimental uncertainties.

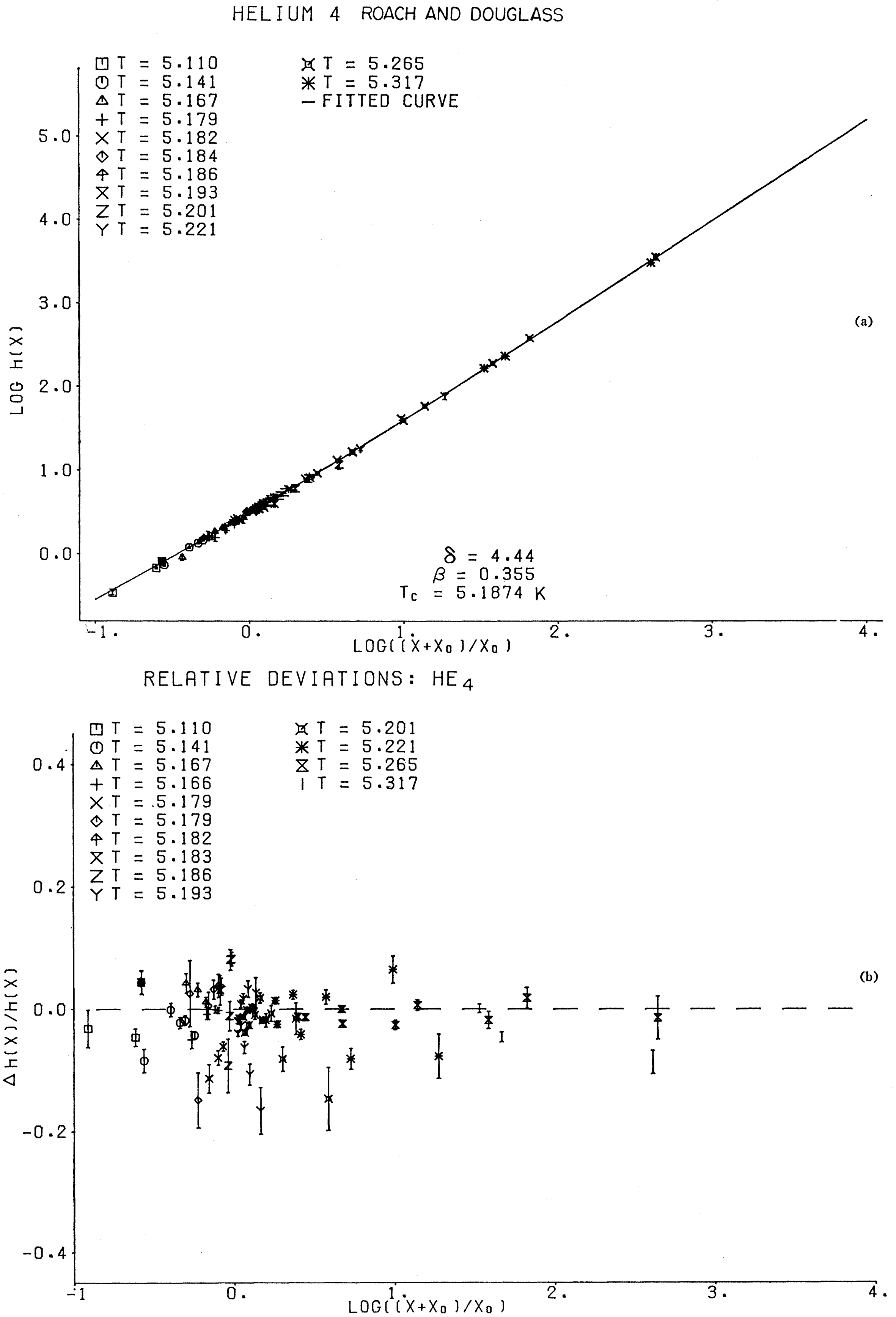


FIG. 7. (a) Log-log plot of $h(x)$ versus $(x+x_0)/x_0$ for He^4. Solid line is fitted function [Eq. (12)] with parameters given in Table II. Experimental points are shown with estimated error bars on variable $h(x)$. (b) Plot of $\Delta h(x)=\{[h(x)]_{\text{expt}}-[h(x)]_{\text{fitted}}\}/[h(x)]_{\text{expt}}$ versus $\log[(x+x_0)/x_0]$ for He^4. Vertical error bars represent estimated limits that include all experimental uncertainties.

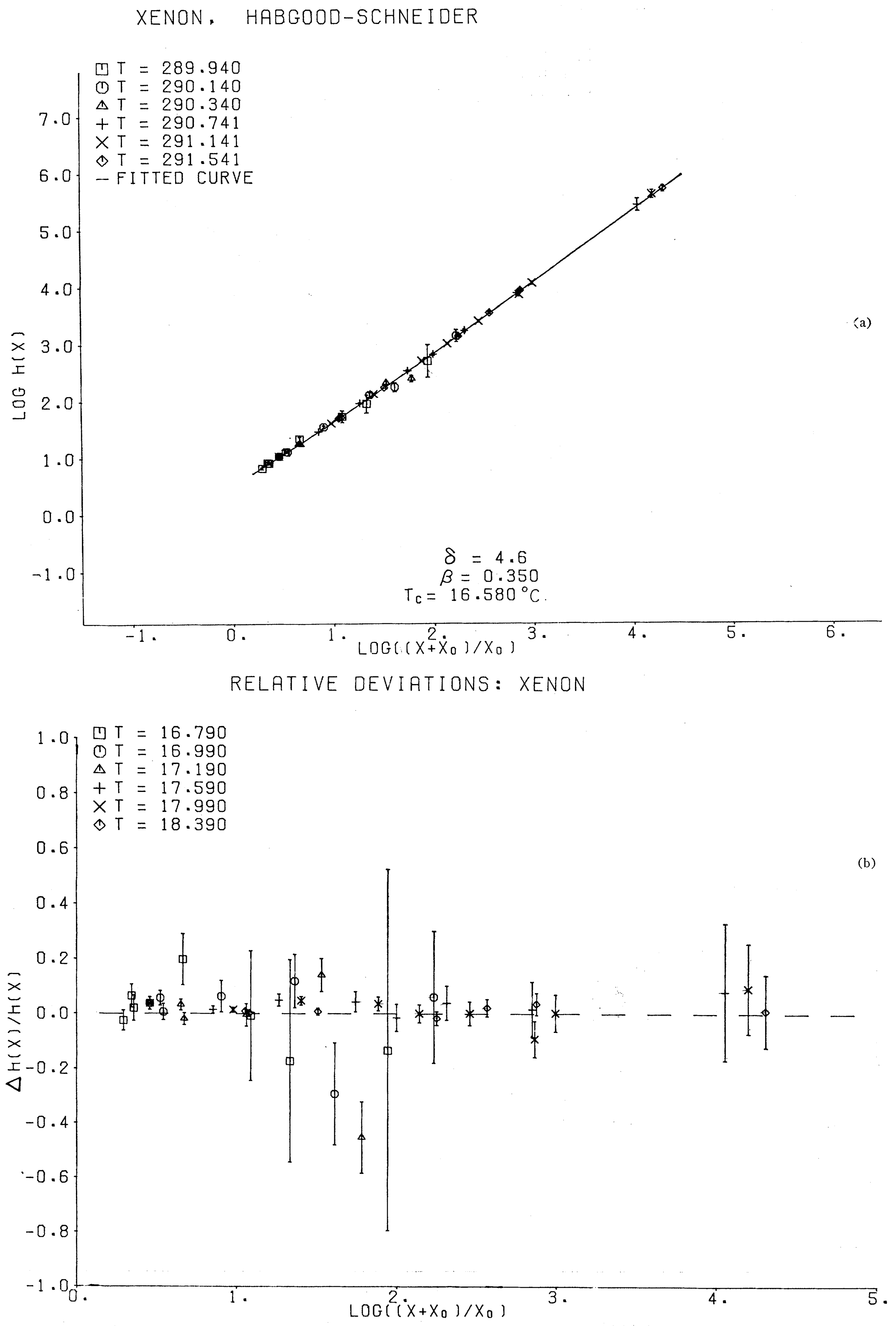


FIG. 8. (a) Log-log plot of $h(x)$ versus $(x+x_0)/x_0$ for Xe. Solid line is fitted function [Eq. (12)] with second set of parameters given in Table II. Experimental points are shown with estimated error bars on variable $h(x)$. (b) Plot of $\Delta h=\{[h(x)]_{\mathrm{expt}}-[h(x)]_{\mathrm{fitted}}\}/[h(x)]_{\mathrm{expt}}$ versus log $[(x+x_0)/x_0]$ for Xe. Vertical error bars represent estimated limits that include all experimental uncertainties.

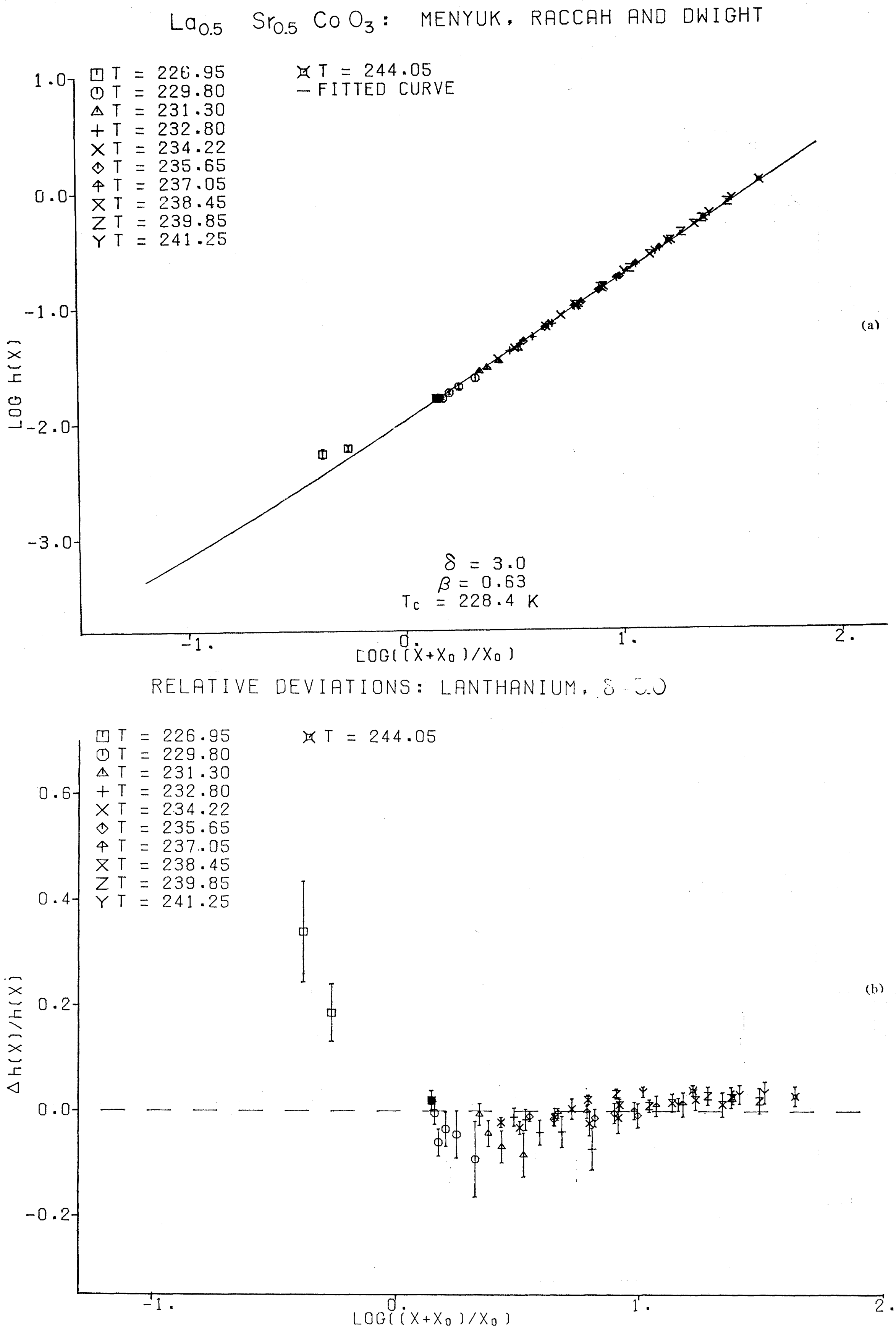


FIG. 9. (a) Log-log plot of $h(x)$ versus $(x+x_0)/x_0$ for $La_{0.5}Sr_{0.5}CoO_3$. Solid line is fitted function [Eq. (12)] for $\delta=3, \beta=0.63$, and other parameters as given in Table II. Experimental points are shown with estimated error bars on variable $h(x)$. (b) Plot of $\Delta h(x)=\{[h(x)]_{\mathrm{expt}}-[h(x)]\}/[h(x)]_{\mathrm{expt}}$ versus $\log[(x+x_0)/x_0]$ for $La_{0.5}Sr_{0.5}CoCO_3$ [$\delta=3, \beta=0.63$]. Vertical crror bars represent estimated limits that include all experimental uncertainties.

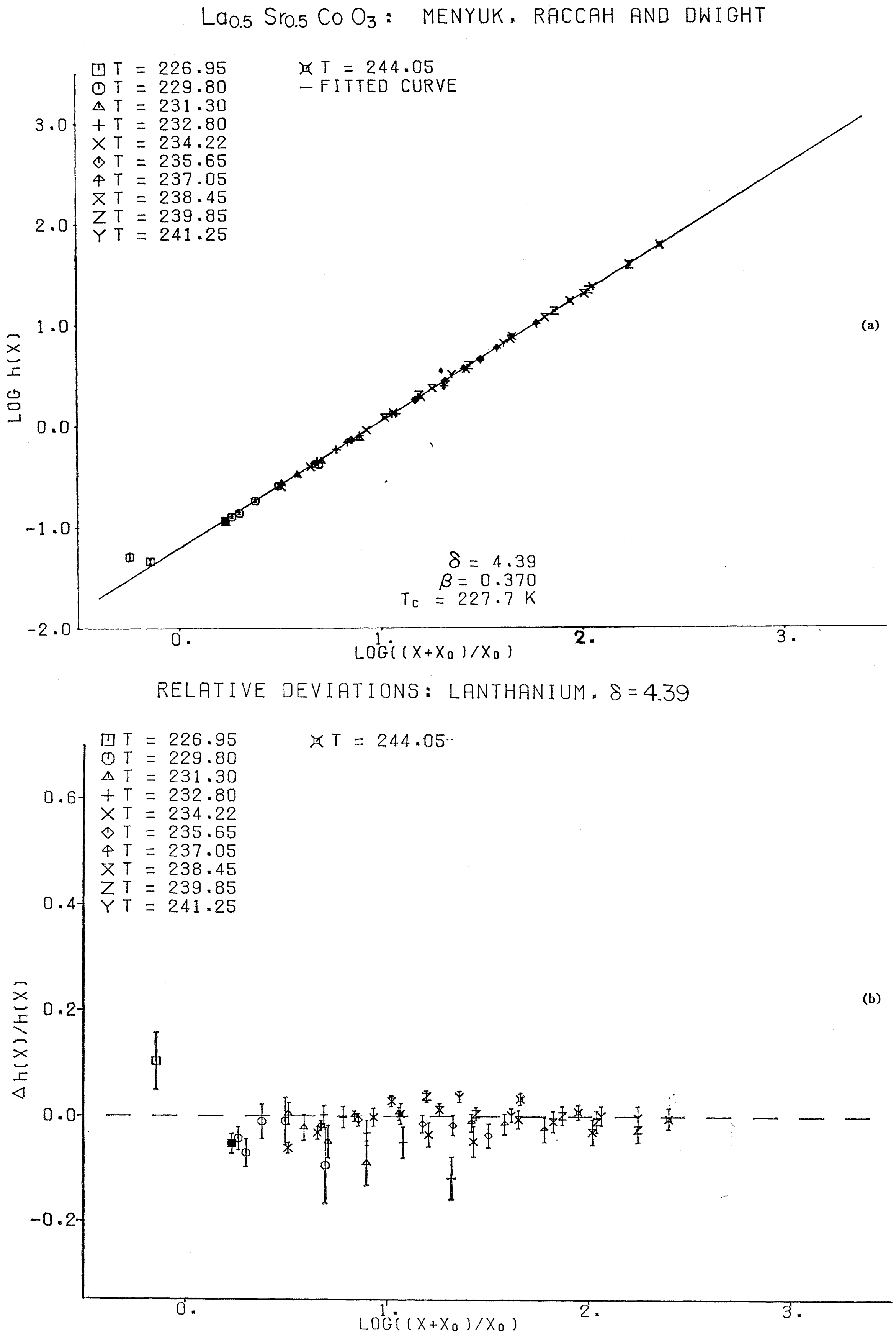


FIG. 10. (a) Log-log plot of $h(x)$ versus $(x+x_0)/x_0$ for $La_{0.5}Sr_{0.5}CoO_3$. Solid line is fitted function [Eq. (12)] for $\delta=4.4, \beta=0.37$ and other parameters as given in Table II. Experimental points are shown with estimated error bars on variable $h(x)$. (b) Plot of $\Delta h(x)=\{[h(x)]_{\text{expt}}-[h(x)]_{\text{fitted}}\}/[h(x)]_{\text{expt}}$ versus $\log[(x+x_0)/x_0]$ for $La_{0.5}Sr_{0.5}CoO_3$ [$\delta=4.4$ $\beta=0.37$]. Vertical error bars represent estimated limits that include all experimental uncertainties.

TABLE III. Comparison for $CrBr_3$ of coefficients of series expansion of $h(x)$ on critical isotherm (h_0,h_1,h_2) and critical isochore $(\eta_1,\eta_2,\eta_3,\xi_1)$.

	h_0	h_1	h_2	η_1	η_2	η_3	ξ_1
Ho and Litster[a]	0.63±3%	1.14±5%	0.20±25%	0.89±1%	0.85±6%	0.23±20%	···
Present	0.638	1.15	0.11	0.91	0.28	···	0.65

[a] Reference 17.

is concerned, as well as the values of x_0 and T_c, our function gives quite reasonable values. Furthermore, if the systematic deviations of Fig. 2(b) are significant, they do not bias this result.

It is also difficult to make any general statement about the presence of systematic deviations from the proposed function $h(x)$ [Eq. (12)] as a function of x. What might appear to be a trend shows up only in the two sets of Ni data. However, the consistency checks discussed in detail below make us confident that the values of the parameters derived for this material from this function are reliable.

The parameters determined by our method of fitting the experimental data, where successful, are given in Table II. For the reasons discussed previously in the case of $La_{0.5}Sr_{0.5}CoO_3$, we have listed the two sets of values we tried. The numbers in parentheses for the magnets are the results obtained from independent analysis of the data by the listed authors. For the fluids they are the results given by the four-parameter fit discussed in Ref. 6. In general, the agreement is quite reasonable. The value of γ given in the table was obtained by use of Eq. (11).

In the case of Gd the present values differ from the approximate values obtained previously[15,24] because of what we feel is a more precise determination of T_c.

The differences between our values of γ and δ for Ni and the values given by Kouvel and Comly[14] require detailed discussion since the values of the critical temperature are in precise agreement. We will do this by a detailed comparison of the results of our analysis with the experimental data on the three preferred curves, critical isochore, critical isotherm, and phase boundary. This comparison is shown in Fig. 11. In each part of this figure the solid line is the behavior predicted by our analysis. The points are the directly measured H, M data for the critical isotherm, or in the other two cases, the results of an extrapolation made by Kouvel and Comly. The agreement is good except for the points on the critical isochore at low values of t. The slope of the solid line [Fig. 11(a)] corresponds to the value $\gamma=1.28$, while a line through the points yields $\gamma=1.34$. In order to understand the disagreement, in Fig. 12 we show an M^2-versus-H/M plot for the lower isotherms. The various symbols are the experimental points, the dashed lines represent the extrapolation assumed in deriving

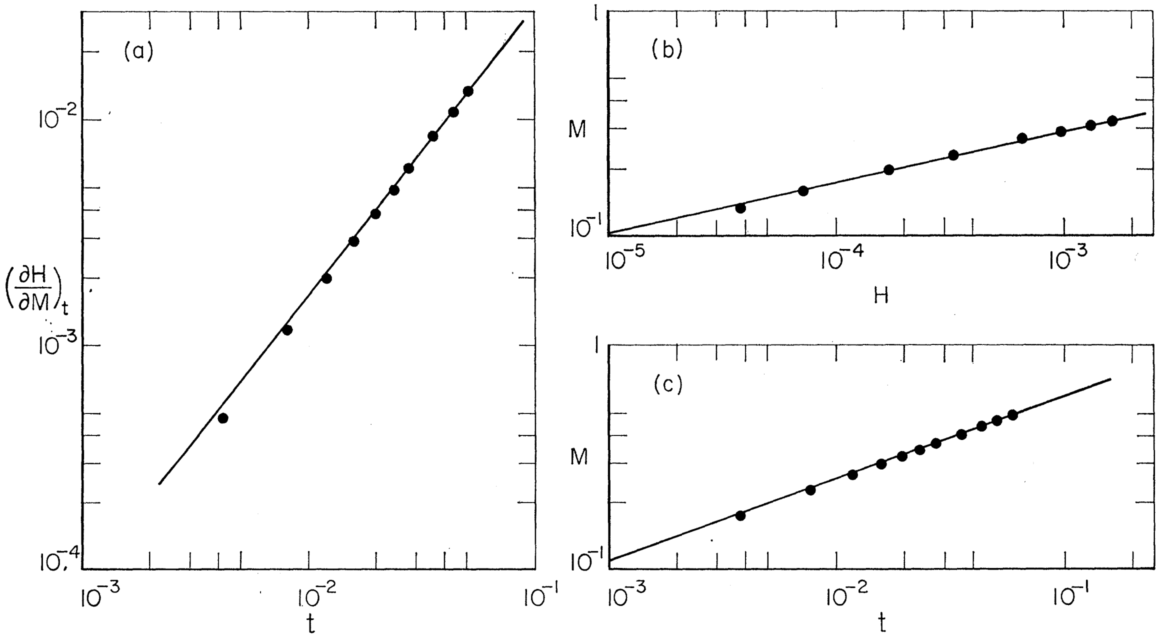


FIG. 11. Comparison of predicted (solid lines) and experimental behavior of Ni (Ref. 14) on the preferred curves: (a) critical isochore, (b) critical isotherm, and (c) phase boundary.

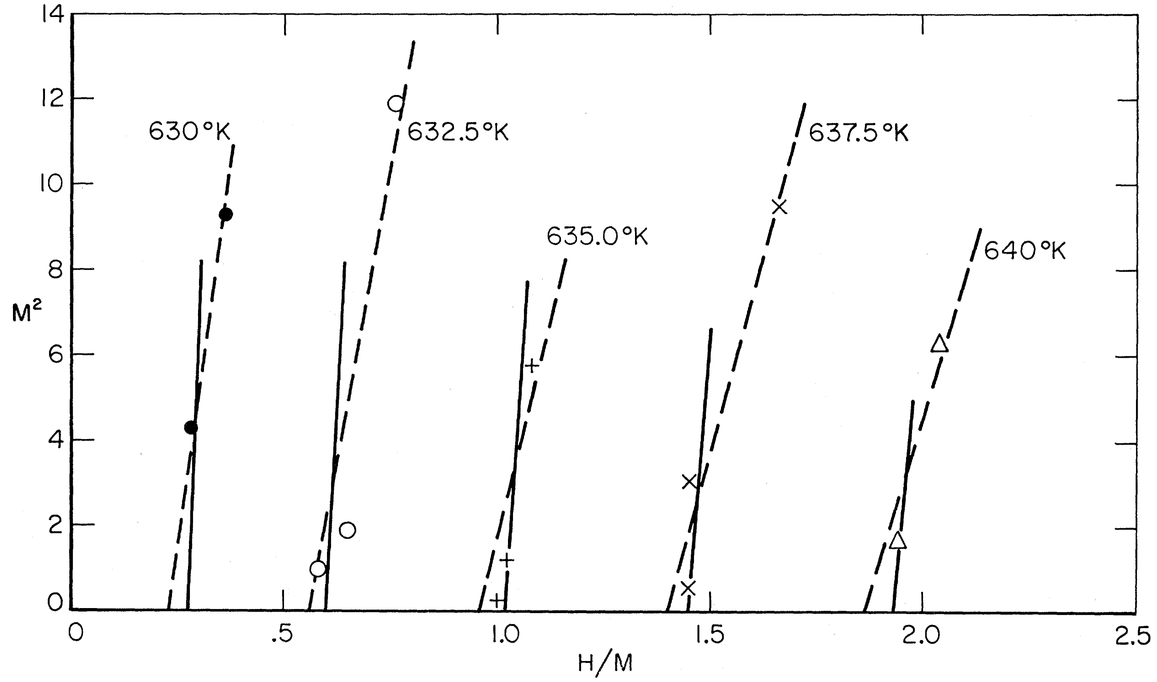


FIG. 12. Plot of M^2 versus H/M for isotherms close to critical in Ni (Ref. 14). Symbols are experimental points, dashed lines are based on a linear extrapolation procedure (Ref. 14), and solid lines are asymptotic behavior at $M=0$ according to Eq. (12) using parameters given in Table II.

the points in Fig. 11(a), and the solid lines represent the asymptotic slopes at $M=0$ that one would need to observe in order to obtain the values of the susceptibility predicted by our analysis. It is clear that the difference in the susceptibility is due to the different extrapolation procedures. We recall that for isotherms quite close to critical the linear region is confined to small values of M and hence the KF extrapolation procedure has an inherent limitation as one gets asymptotically close to the critical temperature. On the other hand, our method of calculating the susceptibility uses a function which for large x, while not having the exactly correct series expansion, still predicts a linear dependence of H/M on M^2 to lowest order. We feel that the present method of proceeding has the advantage of making use of considerably more of the available data than just those at low magnetizations which have the greatest experimental uncertainties. It also agrees with the results of the KF method at large t where this method is more rigorous. Very accurate measurements at small M, especially when T is very close to T_c, are needed to decide on the correct extrapolation procedure.

Analysis of the more recent data on Ni obtained by Kouvel and Comly[14] yield a value of δ considerably different from that obtained by Kouvel and Fisher[10] from the data of Weiss and Forrer.[13] However, a critical analysis of the consistency between the two sets of data shows that they agree, except for a shift of about 0.8 K in the temperature scale (the scale of Weiss and Forrer[13] is lower than the scale of Kouvel and Comly). One should therefore expect to see a difference of the same magnitude and sign in the absolute values of the critical temperatures obtained from these two sets of data. Actually our analysis applied to the two sets of data yields a difference in the critical temperature of 0.9 K in the right direction. All other parameters are the same within their error bounds. However, for the data of Weiss and Forrer the analysis of Kouvel and Fisher gives for T_c a value only 0.2 K lower than the value obtained for the data of Kouvel and Comly. The low value of δ derived by Kouvel and Fisher for the Weiss data is then simply explained by the fact that they obtain this value by considering an isotherm slightly above critical.

For $La_{0.5}Sr_{0.5}CoO_3$ comparison of the deviation plots for the two sets of values of β and δ we have used, Fig. 9(b) ($\beta=0.63$, $\delta=3$) and Fig. 10(b) ($\beta=0.37$, $\delta=4.4$), shows that if anything can be said, the result for the latter case is slightly better. However, we feel that the experimental data are insufficient to determine accurately the exponents β and δ. The value of the exponent γ derived from our analysis is in agreement with that previously obtained. In the present situation it is determined from isotherms with large values of t so that the critical temperature is poorly found by the KF method. If we try to get an indication of the value of T_c from a study of the behavior of the three isotherms which should be closest to critical, such as is shown in Fig. 13, we can only conclude from the observed curva-

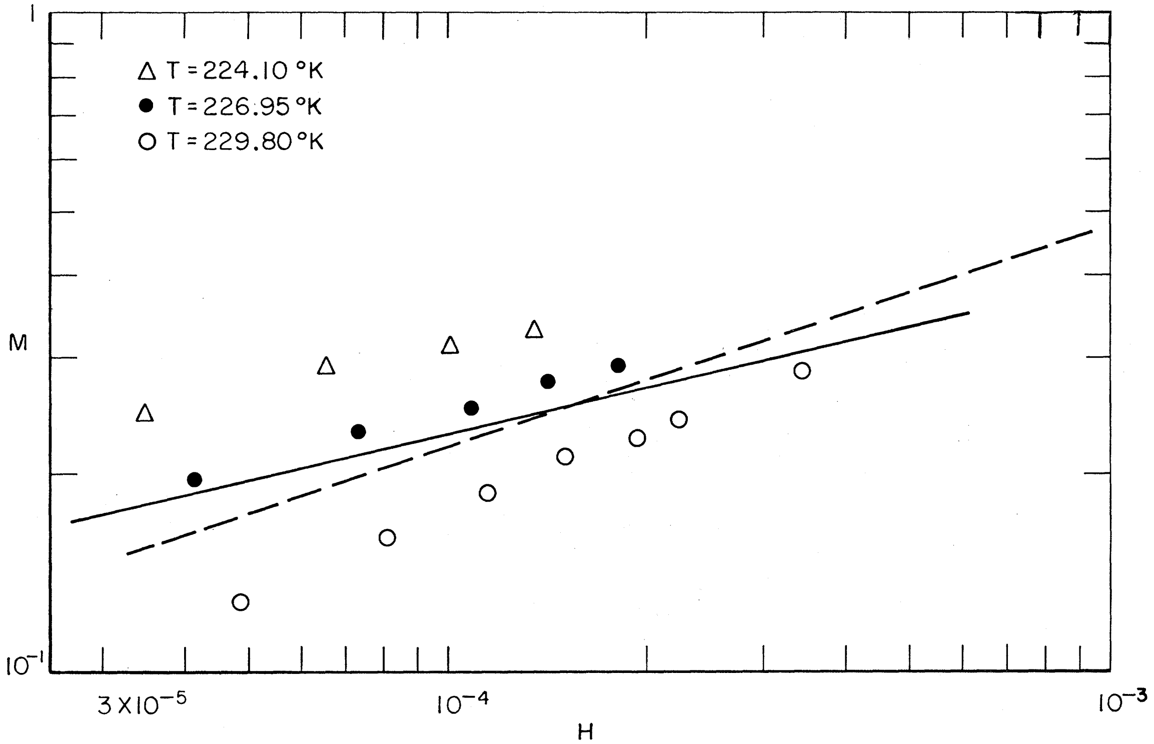


FIG. 13. Comparison of experimental value of M versus H on a log-log scale for three isotherms close to the probable critical temperature in $La_{0.5}Sr_{0.5}CoO_3$ with predicted behavior according to fit of Eq. (12) with $\delta=3$ (dashed line) and $\delta=4.4$ (solid line).

ture in the isotherm at 229.8 K that $T_c<229.8$ K, the other two isotherms showing no significant curvature in either direction. For the sake of comparison we also show in this figure our computed behavior of the critical isotherm for the two cases we considered, $\delta=3$ (dashed line) and $\delta=4.4$ (solid line). It is clear that neither is in good agreement with the data. Until additional data closer to the critical point are taken, no definite conclusion can be obtained for this substance. It is, however, true that the same values of β and δ found for the other magnetic materials considered can adequately describe the critical-point behavior of $La_{0.5}Sr_{0.5}CoO_3$.

For the fluids the only significant difference in the parameters as determined by the present multiparameter fit and the previous four-parameter fit,[6] in which β and x_0 were assumed known, is the difference between the two values of δ for CO_2. We believe that this is due to the fact that for this substance the amount of experimental information very close to the critical isotherm is scarce and that more experimental data are needed to get an accurate estimate of δ. The indication is, however, that δ is closer to 4.5 than it is to 4.6.

The previous discussion of the results of the present analysis for the case of the critical behavior of $CrBr_3$ leads us to the conclusion that the present method permits us to assign reliable values not only to the parameters β, δ, T_c, and x_0 but also to the derived parameters B, Δ, Γ, and Γ' defined in Eqs. (1)–(4), respectively. Hence we have assumed this to be true in every case in which the amount of experimental information is such that the multiparameter fit unequivocally indicates a best fit, that is, in all cases considered in detail except $La_{0.5}Sr_{0.5}CoO_3$. These derived parameters are listed in Table IV. We have also listed there the values of the ratio Γ/Γ' which we note appears to be roughly constant and of order 3 for all the magnets while for all the fluids it is roughly constant and of order 4.

Other parameters which can be derived from a knowledge of the function $h(x)$ are the parameters which describe the behavior of the specific heat. We have seen that an equation of state based on scaling ideas gives a good representation of the data in the critical region for both the fluids and the magnets. For the behavior of the

TABLE IV. Parameters characterizing phase boundary, critical isotherm, and susceptibility on the critical isochore.

	B	Δ	Γ^{-1}	$(\Gamma')^{-1}$	Γ/Γ'
$CrBr_3$	1.20	0.638	0.91	2.75	3.0
Gd	1.16	0.88	1.14	3.15	2.7
Ni[a]	1.44	0.238	0.61	1.80	2.9
Ni[b]	1.46	0.230	0.62	1.79	2.9
CO_2	2.01	2.32	16.3	67.5	4.2
Xe	1.80	3.3	16.9	70.0	4.1
He^4	1.441	3.14	7.16	26.9	3.8

[a] Reference 14.
[b] Reference 13.

TABLE V. Exponent α as derived from values of β and δ by use of Eq. (10).

$CrBr_3$	Gd	Ni[a]	Ni[b]	CO_2	Xe	He^4
$+0.06\pm0.06$	$+0.01+0.09$	-0.03 ± 0.15	-0.05 ± 0.13	$+0.06\pm0.09$	$+0.04\pm0.09$	$+0.06\pm0.09$

[a] Reference 14.
[b] Reference 13.

specific heat this implies that α must be equal to α'. Since there is no clear cut indication from direct measurements of the nonanalytic part of the specific heat[26–29] that this is not true, we shall assume this property to be satisfied. From our derived values of β and δ we can then derive values for α by means of Eq. (10), and these are presented in Table V. The uncertainty in the values of α is quite large. For the fluids the indication is that α is positive, and a value of 0.04 is acceptable for the three substances considered. For the magnets α seems to be clearly positive only for $CrBr_3$. However, for the present purposes, a value of $\alpha=+0.02$ is acceptable for $CrBr_3$, Gd, and Ni. A property of the specific heat which does not appear to be too sensitive to the value of α is the coefficient Δ_c of Eq. (7) which describes the jump in the specific heat across the phase boundary. This quantity can be calculated[4,6] simply from $h(x)$ by[30]

$$\Delta_c=\beta x_0^{\alpha-1}h'(-x_0). \tag{17}$$

On the other hand, once α is known the coefficients A^+ and A_{II}^- of Eqs. (5) and (6), respectively, can be numerically evaluated from $h(x)$[4,6]:

$$A_+=\alpha\beta\int_0^\infty dy\, h''(y)y^{\alpha-1}, \tag{18}$$

$$A_{\text{II}}^-=\alpha\beta\left[\int_{-x_0}^0 dy\, h''(y)\,|y|^{\alpha-1}+x_0^{\alpha-1}h'(-x_0)\right]. \tag{19}$$

Their value is quite sensitive to the value of α. Values of Δ_c, A^+, and A_{II}^- calculated in this way are given in Table VI for a typical value of α, specifically $\alpha=+0.02$ for the magnets and $\alpha=+0.04$ for the fluids. To show the dependence of these quantities on α we have also shown for one of the Ni cases the derived value for different choices of $\alpha(\pm0.06)$.

TABLE VI Parameters describing behavior of specific heat on the critical isochore.

	α	Δ_c	A_{II}^-	A^+
$CrBr_3$	0.02	0.54	0.092	0.078
Gd	0.02	0.57	0.15	0.13
Ni[a]	0.02	0.49	0.13	0.11
Ni[b]	-0.06	0.54	0.09	0.15
	$+0.02$	0.50	0.15	0.13
	$+0.06$	0.48	0.17	0.13
CO_2	0.04	42	6.3	4.6
Xe	0.04	28	4.8	3.6
He^4	0.04	7.3	1.4	1.06

[a] Reference 14.
[b] Reference 13.

4. DISCUSSION

We find that the experimental data in the critical region of both the magnets and fluids satisfy the scaling properties which have been theoretically suggested to be valid in that region. In all cases the proposed form for the scaled function $h(x)$ [Eq. (12)] fits the data within the estimated uncertainties and it can be used to determine values for the critical exponents β and δ. The same form for the equation of state thus appears to describe the critical point of fluids and the Curie point of ferromagnets. There are differences however between the two groups of substances. While the exponent β appears to be reasonably constant within either group, it seems to be systematically lower for the fluids (0.352) compared to the magnets (0.370). Furthermore, the ratio Γ/Γ' is the same for all fluids and about 4, while for the magnets $\Gamma/\Gamma'\simeq3$. The parameter x_0 seems to be a characteristic of the particular substance considered. In regard to the exponent δ, there is very scant evidence of it being significantly different between the fluids and magnets, a value of 4.4 being consistent with all our results. More precise data on a larger number of materials are needed to reach a definite conclusion on this point. However, we have shown that there are serious reasons to question the values for β and δ largely different from 0.37 and 4.4, respectively, that have been reported in the literature ($La_{0.5}Sr_{0.5}CoO_3$: $\beta=0.63$, $\delta=3.05$; $YFeO_3$: $\beta=0.55$, $\delta=2.78$; CrO_2: $\beta=0.34$, $\delta=5.75$) as being representative of the true asymptotic behavior.

The explicit form for the equation of state at the critical point which we have proposed gives a good representation for the entire range of the variable $x\,(-x_0<x<\infty)$.

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[26] B. J. C. van der Hoeven, D. T. Teaney, and V. L. Moruzzi, Phys. Rev. Letters **20**, 719 (1969).

[27] P. Handler, D. E. Mapother, and M. Rayl, Phys. Rev. Letters **19**, 356 (1967).

[28] M. R. Moldover, Ph.D. thesis, Stanford University, 1966 (unpublished).

[29] C. Edwards, J. A. Lipa, and M. J. Buckingham, Phys. Rev. Letters **20**, 496 (1968).

[30] If $\alpha=0$, a constant jump should be observed, while for $\alpha\neq0$ the jump would be a function of temperature which diverges at $t=0$ if $\alpha>0$ but decreases to zero at $t=0$ if $\alpha<0$. Measurements of this quantity should be a very sensitive means of determining the sign of α.

While the higher-order terms in the series expansion of this function do not have the correct form at large x, a detailed comparison with the results of the analysis of Ho and Litster,[17] who used the first three terms in the exact expansion, showed that the values of the exponents and of the most important coefficients in the critical region are not significantly affected by the inadequacies of our function. It is instructive to compare our proposed form for the function $h(x)$ [Eq. (12)] with that proposed by Arrott and Noakes[31]

$$h_{\mathrm{AN}}(x)=(x+x_0)^{\beta(\delta-1)} \tag{20}$$

and an alternate one proposed by Ho and Litster[17]

$$h_{\mathrm{HL}}(x)=A(x+x_0)(x+C)^{\beta(\delta-1)-1}. \tag{21}$$

It is readily seen that both of these functions behave badly at large x. The leading term in the appropriate expansion goes as x^{γ}, but the next term is of the wrong form, $x^{\gamma-1}$. In terms of the variables H/M and M^2 the expansions of these two functions for small M are of the form $H/M=a'+b'(M^2)^{1/2\beta}$ instead of the correct form $H/M=a+bM^2$. In the case of the function we have used, a term of the form bM^2 is present, the third term being of the form $b'(M^2)^{1/2\beta}$; that is, the incorrect term appears as a second-order term in our case, while in the other two functions it appears in first order.

The function we have proposed predicts a nonanalytic behavior at the phase boundary which could, if desired, be readily removed by inclusion of an additional parameter—for example, replace the quantity in the curly brackets of Eq. (12) by $1+[(x+x_0')/x_0]^{2\beta}$. Considering the present status of the available experimental data, it hardly seems necessary to introduce another undetermined parameter. Such a parameter would be important only very close to the phase boundary, where extensive experimental information is not available. The function proposed by Arrott and Noakes has an infinite susceptibility on the phase boundary.

The function $h(x)$ we have used predicts the existence of a spinodal, defined as a value of $x(x_1)$ inside of the two-phase region, for which the susceptibility would diverge,

$$\beta\delta h(x_1)=x_1h'(x_1). \tag{22}$$

Numerical solution of this equation shows that for the fluids $x_1/x_0\cong-3.1$, while for the magnets $x_1/x_0\cong-3.4$ (in the mean-field approximation the spinodal occurs at $x_1/x_0=-3$).

Fisher[32] has recently developed a theory of the "renormalization of critical exponents by hidden variables." It is there suggested that the observed critical exponents α_x, β_x, γ_x are related to the "ideal" exponents α, β, γ by

$$\alpha_x=-\alpha/(1-\alpha), \tag{23}$$

$$\beta_x=\beta/(1-\alpha), \tag{24}$$

$$\gamma_x=\gamma/(1-\alpha), \tag{25}$$

with similar relations for the primed exponents. If the scaling relations are assumed valid, it follows that primed and unprimed exponents are identical and the renormalized and ideal exponents δ are equal,

$$\delta_x=\delta. \tag{26}$$

The ideal exponent $\alpha'=\alpha$ is assumed here to be positive. Now, in the context of this theory, if we conclude from our results that δ is the same for both fluids and magnets, together with the experimental indication that α_x for the fluids is positive, then the exponents for the fluids would correspond to the ideal situation and the exponents for the magnets represent renormalized values. From our results for β a value of $+0.05$ is obtained for the ideal exponent α which is in good agreement with the observed divergence of the specific heat of fluids and the values given in Table V. For the magnets the observed α would then be negative, which is not inconsistent with the values of α we have presented in Table V.

ACKNOWLEDGMENTS

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[31] A. Arrott and J. E. Noakes, Phys. Rev. Letters **19**, 786 (1967).

[32] M. E. Fisher, Phys. Rev. **176**, 257 (1968).